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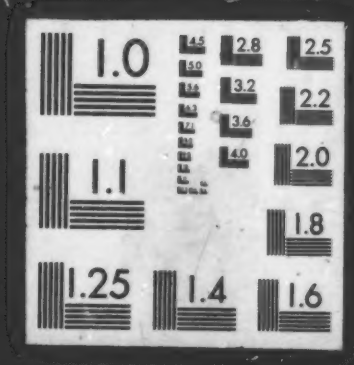

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Atmospheric particles were collected from May, 1980 to Dec., 1981 at 3 sampling sites in the Ohio River Valley (ORV). The collected samples were analyzed by x-ray fluorescence (XRF) for elemental concentrations and their masses determined by β gauging. The XRF data and associated wind trajectories were used to select a subset (200) of ORV samples in the fine fraction for further analysis by instrumental neutron activation analysis (INAA). Combined XRF and INAA data provided concentration values for up to 40 elements. Trace element concentration ratios to Se did not show modal distributions which were previously observed in samples collected downwind from the Midwest U.S. Chemical mass balances with 11 sources are being used to fit trace element concentrations.

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Most particulate S is governed by the regional sulfate component. Results suggest that the distance scale is shorter than previously thought.

INTRODUCTION

Trace element compositions of airborne particles are important for determining sources and behavior of regional aerosol, as emissions from major sources are characterized by their elemental composition patterns. We have investigated airborne trace elements in a complex regional environment through application of receptor models. A subset (200) of fine fraction samples collected by Shaw and Paur (1) in the Ohio River Valley (ORV) and analyzed by x-ray fluorescence (XRF) were re-analyzed by instrumental neutron activation analysis (INAA). The combined data set, XRF plus INAA, was subjected to receptor-model interpretations, including chemical mass balances (CMBs) and factor analysis (FA). Back trajectories of air masses were calculated for each sampling period and used with XRF data to select samples to be analyzed by INAA.

EXPERIMENTAL METHODS

Sampling Sites. The 3 ORV sampling sites (see Fig. 1) were selected in rural areas having minimal effects of local sources. The west site was in a rural farming community in Union County, KY, the center site in a similar area of Franklin County, IN, and the east site was in a forest clearing in Ashland County, OH. The sites lie along a 590-km line with roughly equal spacings between them.

Sampling Procedures and Analyses. Samples were collected from May, 1980 to Dec., 1981 using dichotomous samplers which separated particles into two size fractions (cut-point at 2.5-μm diam). Particles were collected on 1-μm pore-diam Teflon membrane filters. Details of the sampling protocol are discussed elsewhere (1). Sampling periods were

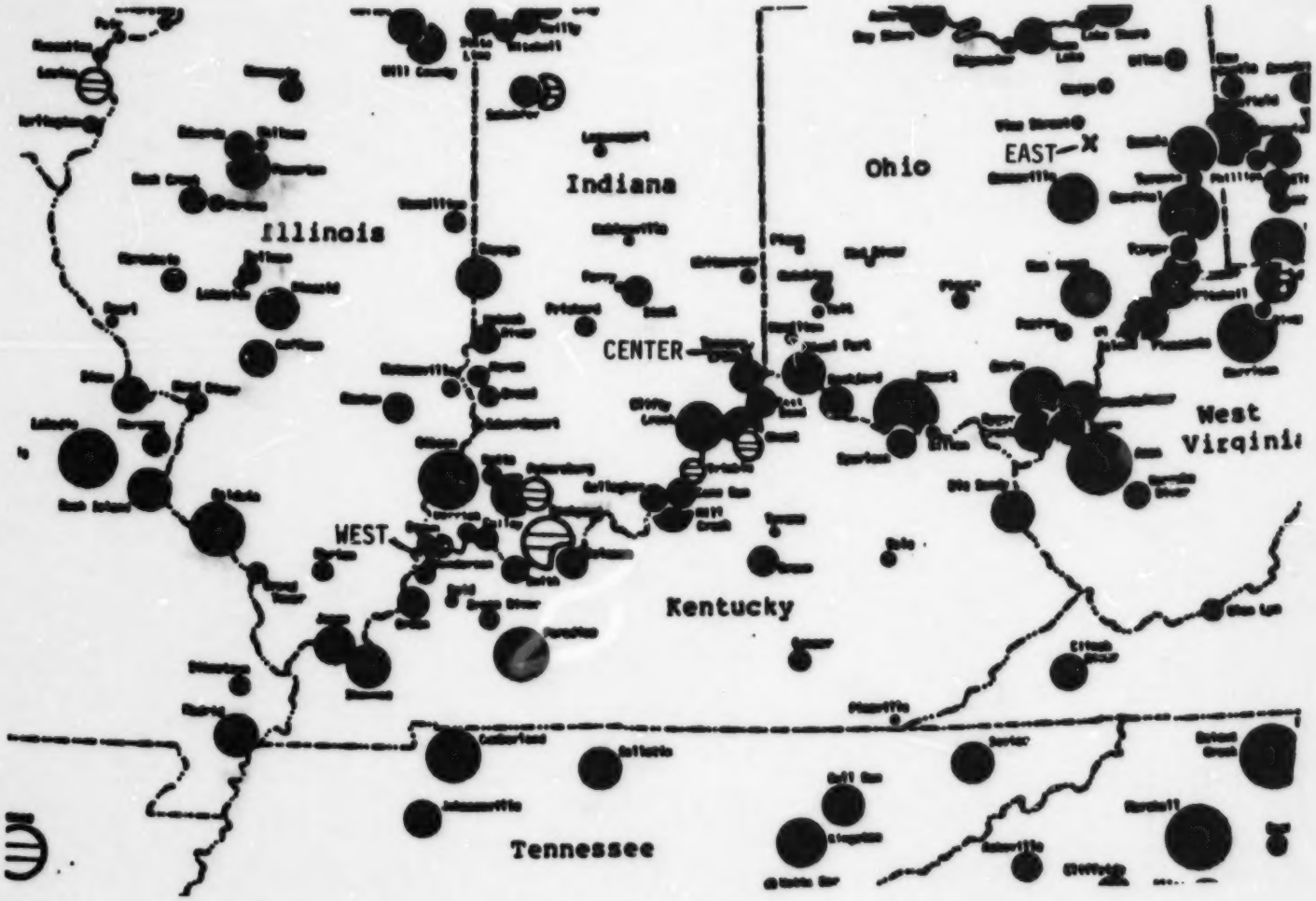

Fig. 1. Map of Ohio River Valley showing ORV sites (X) and coal-fired power plants, with sizes of circles indicating relative capacities.

12 h for some samples, but 24 h for most, with samples being changed at 8 am and 8 pm for the former, and midnight for the latter.

Following ß-gauging for mass determination and XRF analyses at Environmental Sciences Research Laboratory (ESRL), samples were sent to the University of Maryland. The samples were opened in a Class 100 clean room and half of each filter was cut from the holder with a stainless steel scalpel, folded and transferred to an acid-washed polyethylene bag. The bags were placed into pneumatic tube sample carriers ("rabbits") along with standards and flux monitors, and irradiated in the National Bureau of Standards (NBS) reactor at a flux of 5×10^{13} n/cm^2-sec. Gamma-ray spectra of the irradiation products were observed with Ge γ-ray detectors using procedures discussed by Germani et al. (2). The final data selected are from INAA except for Br, S, Si and Pb, taken from XRF. The combined methods yield data for about 40 elements.

RESULTS AND DISCUSSION

Trajectory Groups. Back-trajectories of air masses were calculated for each sampling period using the Air Resources Laboratory Branching Atmospheric Trajectory model (3). We classified sampling periods according to the directions of their associated back-trajectories as was done previously with Shenandoah Valley samples (4). Shaw and Paur (1) found that the average particulate concentration is about the same at the 3 ORV sites despite the classical picture of the build-up of sulfate from conversion of SO_2 as air masses move up the Valley towards the Northeast. We suspected that the constancy of particulate S might result from occasional movement of heavily laden air masses back from the east. However, Table 1 shows that, even when we consider only air masses from the southwest, the center site has the highest average

Table 1. Concentrations of Selected Elements in Fine Fraction at Three ORV Sites in Air Masses with Southwest Back Trajectories

Element	Concentration (ng/m³)[a]		
	West Site (n = 16)	Center Site (n = 14)	East Site (n = 23)
Na	110 ± 60	70 ± 40	90 ± 60
Al	180 ± 170	150 ± 120	110 ± 180
Si	570 ± 520	360 ± 240	230 ± 340
S	2500 ± 1400	4100 ± 1600	3400 ± 2600
Cl	30 ± 90	35 ± 21	50 ± 55
K	120 ± 50	115 ± 50	90 ± 65
Ca	105 ± 70	80 ± 30	55 ± 35
Sc	0.04 ± 0.04	0.03 ± 0.02	0.09 ± 0.14
V	1.4 ± 0.8	0.8 ± 0.5	0.8 ± 0.6
Mn	18 ± 17	4.7 ± 1.3	7 ± 8
Fe	140 ± 115	90 ± 50	120 ± 240
Zn	11 ± 6	14 ± 6	26 ± 19
As	0.9 ± 0.5	0.9 ± 0.4	1.4 ± 1.3
Se	1.9 ± 0.8	1.9 ± 0.7	2.0 ± 1.3
Br	4.1 ± 2.0	4.9 ± 1.5	6 ± 4
In	0.01 ± 0.009	0.01 ± 0.01	0.06 ± 0.2
Sb	0.6 ± 0.5	0.5 ± 0.2	0.6 ± 0.4
La	0.27 ± 0.25	0.2 ± 0.14	0.12 ± 0.11
Sm	0.03 ± 0.02	0.02 ± 0.01	0.014 ± 0.017
Pb	34 ± 15	53 ± 11	56 ± 22

[a]Uncertainties are standard deviations of a single observation

S concentration, and that of the west site is only ~30% below that of the east site. Thus, there is not a strong build-up of particulate S as air masses move towards the northeast. Indeed, comparison of Fig. 1 with the results discussed above suggests that SO_4 levels are strongly influenced by the density of coal-fired plants immediately upwind of the sampling site on a distance scale of the order of about 300 km, rather than the many 100s of km required to transport SO_4 from the ORV to New England. To make a more quantitative statement, we would need to perform hybrid receptor modeling, which relates concentrations of gas- and particulate-phase S to those of other species associated with sulfur sources, e.g., particulate Se. (5,6).

Regional Signatures. Rahn and Lowenthal (7,8) developed a tracer system based on the assumption that particles from large regions (dimensions of several 100 km) bear characteristic patterns of trace elements. They characterized regional aerosols by the ratios of several trace elements to that of Se: As, Zn, In, Sb and non-crustal V and Mn. "Non-crustal", applied to V and Mn, means that crustal contributions are subtracted based on Al as an indicator of crustal mass. Their model is based on observation of various modes in log normal frequency histograms of the ratios in samples collected at several places. The key assumption of their model is that particles of such a region become so well mixed that, when observed downwind of the region, the samples collected from air masses passing through those regions take on the characteristic ratios to Se. According to the most recent Rahn/Lowenthal paper (8), there are different characteristic ratios for the Upper Midwest (UMW), the region around and just below the Great Lakes, and the Lower Midwest (LMW), mainly the ORV. Average As/Se ratios for these two regions are

1.49 ± 0.60 and 0.23 ± 0.07, respectively. In Fig. 2 is shown a log normal histogram of As/Se ratios observed on all samples analyzed in this work. We see no clear evidence for the predicted bimodal distribution of the As/Se ratio, nor do we observe it for the other elements suggested as tracers. This does not necessarily mean that Rahn and Lowenthal are wrong, as we analyzed selected samples rather than the entire set. Also, we determined the ratios in the Midwest rather than downwind from it, so additional mixing might produce discrete modes.

Factor Analysis. A major objective of this project is to develop regional scale receptor models which would use some of the 40-odd observed species to determine sources or source regions of the particles. As a first step we performed FA on all samples. In contrast to the rather good FA results obtained from similar data from Shenandoah Valley (4), here the results were rather poor. A 5-factor fit to 23 variables in 200 samples accounted for only 57% of the variance. Factor 1 (Pb, Br, Sb, As and Se) is a combined motor-vehicle and general anthropogenic component. Factor 2 (Fe, Si, Al, Sc, La, Sm) is crustal. Factor 3 (S, Se, mass and south wind, with negative Zn) is the "regional sulfate" factor. Notably, this factor contains negligible Mn, suggesting that the Mn observed on this factor in Shenandoah Valley and Watertown, MA (9) results from both sulfate and Mn being brought into the East by the same winds, but not originating from the same sources. As shown in Table 1, samples from the West often contain large amounts of Mn. Only 7% of the Mn is accounted for by the 5 factors. The excess Mn in the Midwest may arise from iron and steel industries. The origin of Factor 4 (Zn, some S, north wind) is unclear. Factor 5 (V, La/Sm ratio and east wind) is the oil-fired plant factor, perhaps with some refinery contribu-

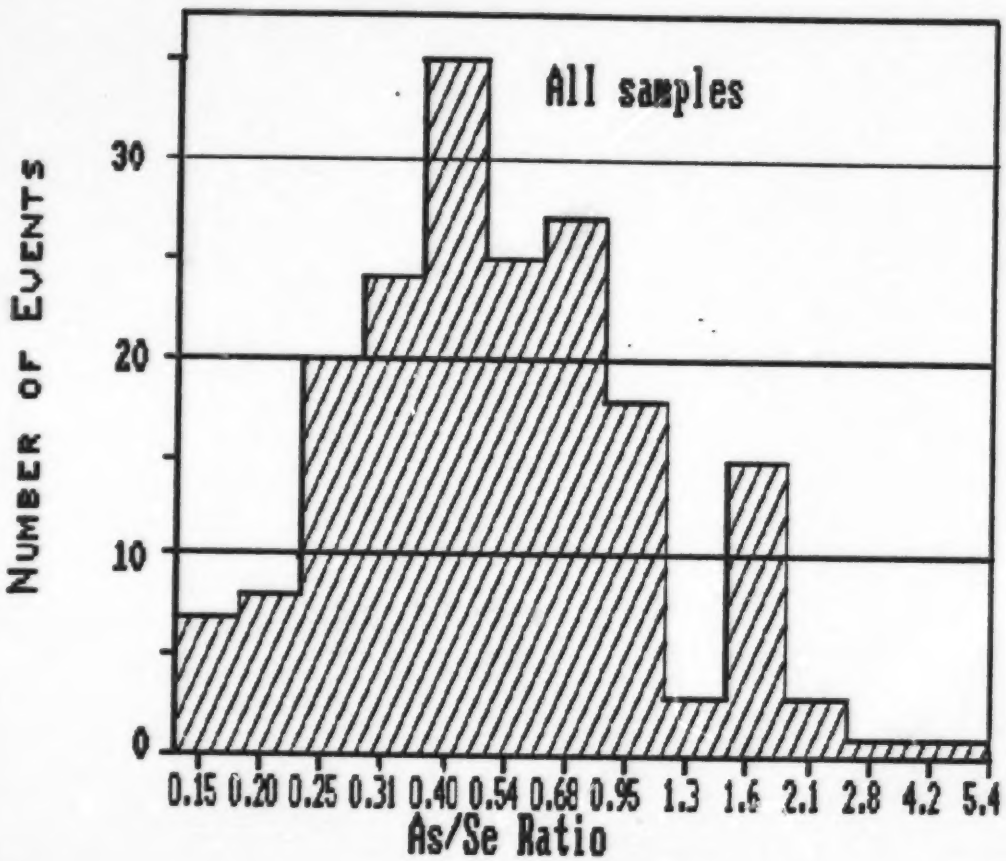

Fig. 2. Histogram of number of observations vs. log As/Se ratios for all samples.

tion (10). The FA results may be poor because samples were pre-selected for certain wind trajectories and/or concentrations from XRF, whereas the entire data set from Shenandoah Valley was used.

Chemical Mass Balances. To attempt a quantitative resolution of the ORV samples, we performed CMBs using 11 components from a source-composition library developed at Maryland (11): coal, oil and refuse combustion, soil and marine aerosol, emissions from refineries, motor vehicles, iron and steel plants, copper plants and lime kilns, and regional sulfate. Some components were modified for this use, e.g., by an increase of Se on the coal component to account for condensation of Se from the vapor phase after stack gases mix with ambient air. Table 2 contains a brief summary of CMBs of ten samples from the east site. The quality of fits is shown by comparison of average predicted and observed concentrations, and by the average larger/smaller (L/S) ratio where, for each sample, L/S for an element is the predicted/observed ratio or its inverse, whichever is larger. A perfect fit for all samples yields an average L/S of 1.00.

Most previous CMBs, e.g., (12), were performed on whole-filter data sets, for which the mass is about half from coarse particles. In this case, many elements arise mainly from crustal dust, making them easy to fit. By contrast, the fine fraction contains little crustal material and many elements are highly enriched (relative to crustal abundances) because of passage through combustion processes. Because of the sensitivity of enrichments to details of the combustion sources and their pollution-control devices, these elements are difficult to fit.

In view of these problems, the fits to the compositions of the

fine fractions are quite good. Only about 80% of the mass is explained, nearly all of it as regional sulfate, but this is typical for fits to fine fractions. The missing mass is probably condensed water and carbonaceous material, nitrates, etc. Magnesium and K are seriously underpredicted, the latter partly because we included no wood-smoke component. The latter would account for residual K, but little else. Chlorine is normally overpredicted, as it is so volatile that it leaves the particles. Titanium is surprisingly underpredicted, but it is not well measured by XRF or INAA in the fine fraction. Several elements, including Cr, Co and Cd may have sources not included in the CMBs, or the components used may be deficient in these elements. A disturbing aspect of the fit is underprediction of heavy rare earths, Eu and Yb, perhaps because of overestimation of refinery contributions, which are enriched in light rare earths.

A major objective of CMBs is to determine primary and secondary contributions from coal-fired plants. Arsenic and Se are often used as "markers" for primary emissions from coal-fired plants (12), but Table 2 shows that substantial amounts of these elements are associated with regional sulfate, most of which results from transport from distant coal-fired plants. The regional sulfate component was based largely on FA of fine particles collected in Shenandoah Valley (4), which mainly represents material transported into the area from the west. At present, we don't know if this component is appropriate for samples collected within the ORV. Also, industrial sources such as copper plants and iron and steel mills interfere with some elements that might otherwise be good markers for coal combustion. Gallium shows promise as such a marker, as does gas-phase B, discussed elsewhere (6). If CMBs can be

Table 2. Summary of CMB Fits to Ten Fine Fraction Samples from East Site

Element	Total Conc. (ng/m3) Predicted	Observed	Avg L/S	Major Sources[a]
Mass(μg/m³)	23.6	30.8	1.7	RegS (22), MV (0.47), Cmt (0.42)
Na[b]	57	56	1.1	Mar (51), Cmt (3), Iron (3)
Mg	16	58	3.2	Mar (6.6), Iron (4.2), Cmt (3.2)
Al[b]	38	36	1.4	Coal (17), Soil (11), Cmt (9)
Si[b]	71	75	1.2	Soil (47), Coal (28), Cmt (19)
S[b]	2500	2310	1.1	RegS (2500), Iron (8), Oil (4)
Cl	103	50	2.8	Mar (93),Incin (8), MV (7)
K[b]	40	61	1.6	Cmt (21), Iron (9)
Ca[b]	57	46	1.4	Cmt (42), Iron (7)
Sc	0.008	0.005	1.8	Coal (0.005)
Ti	2.6	9.2	3.8	Soil (1.2), Coal (1.0)
V[b]	0.80	0.66	1.6	Oil (0.6), Iron (0.4)
Cr	0.22	0.54	3.6	Iron (0.11), Cmt (0.05)
Mn[b]	2.2	2.5	1.3	RegS (1.0), Iron (0.9)
Fe[b]	38	36	1.1	Iron (22), Coal (8), Soil (5)
Co	0.04	0.08	2.9	Oil (0.034), Iron (0.005)
Cu[b]	3.4	5.9	1.8	Cu (2.8), Iron (0.27)
Zn[b]	13	11	1.2	Incin (5), Cu (5)
Ga[b]	0.04	0.09	2.3	Coal (0.02),Cmt (0.014),Iron (0.012)
As[b]	0.34	0.5	1.9	Cu (0.11), RegS (0.11), Coal (0.07)
Se[b]	0.7	1.07	1.7	RegS (0.45), Coal (0.19)
Br[b]	7.8	7.7	1.3	MV (7)
Cd	0.22	0.85	3.4	MV (0.075), Incin (0.06), Cu (0.06)
In	0.004	0.004	3.2	RegS (0.004),Incin & Iron (0.001)
Sb[b]	0.23	0.43	2.1	Incin (0.09), RegS (0.05)
I	0.43	0.63	2.1	Mar (0.29), Coal (0.013)
Cs	0.031	0.027	2.2	Iron (0.025)
La[b]	0.084	0.064	1.6	Ref (0.04)
Ce	0.700	0.080	1.4	Ref (0.034), Coal (0.021)
Sm[b]	0.006	0.008	1.4	MV (0.004), Coal (0.001)
Eu	0.001	0.005	5.7	Coal (0.001)
Yb	0.002	0.014	7.7	Several sources (0.001)
Hf	0.004	0.007	2.5	Soil (0.002)
Pb[b]	43	42	1.1	MV (32), Cu (5)

[a]Numbers in parantheses indicate contributions from indicated source. Abbreviations: Incin = incinerators, Ref = refineries, MV = motor vehicles, Mar = marine, Iron = iron and steel plants, Cu = copper plants, Cmt = cement plants, RegS = regional sulfate.

[b]Included in CMB least-squares fit

used to distinguish between primary and secondary emissions from coal-fired plants, the results can be used in hybrid receptor models to determine important parameters such as the distance scales for transport and transformation of S species.

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